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Shape memory/change effect in a double network nanocomposite tough hydrogel

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ABSTRACT

In this paper, we present a systematic investigation on the shape memory/change effect in a double network nanocomposite tough hydrogel. Water-content dependency of the response of this hydrogel to heating and wetting by water is confirmed. Since this hydrogel is tough (even after being fully wetted in water) and has a relatively lower swelling ratio, apart from conventional shape memory/change effect as in ordinary hydrogels, additional features have been realized. These features include heating induced shape memory effect utilizing the absorbed water as the transition component, mechano-responsive shape change effect after water wetting and water-induced shape memory effect.

1. Introduction

Hydrogel is normally featured by its high volume expansion upon wetting in water (swelling). A number of applications, in particular in biomedical engineering in recent years, have been proposed based on this feature [1–7]. We have seen that great efforts have been dedicated to improve the performance of hydrogels in order to meet the needs of actual applications [2,7–10].

Shape memory effect (SME) refers to the ability of a material to recover its original shape only when the right stimulus, which includes heating/cooling, wetting in water or exposing to high humidity environment etc., is applied [11]. Recent study reveals that the heating/chemo-responsive SME should be the intrinsic feature of many polymeric materials, if not all [12].

Fundamentally, such a SME is different from the shape change effect (SCE), in which the shape of a material changes according to the level of the applied stimulus either proportionally (with/without hysteresis) in a linear/nonlinear manner or gradually in a viscous-elastic way [11,13].

As such, according to above definition, swelling phenomenon itself in hydrogels is essentially under the category of water-responsive SCE. Although the SME has been reported in some purposely synthesized hydrogels [14,15], our recent investigation reveals the water-content dependency of the heating/water (moisture)-responsive shape memory/change effect in a hydrogel and its composites [16]. That is to say, at an extremely low water-content (almost fully dry state), the hydrogel does not have either remarkable mechano-responsive SCE (as it is very stiff and a bit brittle) or the heating-responsive SME

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(since there is no transitions, either the glass transition or melting, as the required condition for the SME); at a relatively lower water-content, it has the heating-induced SME based on the glass transition; at a relatively higher water-content, it becomes rubber-like (mechano-responsive SCE); and at a very high water-content (so that apparent swelling is observed), it shows neither the heating-responsive SME nor the heating-induced SCE. By means of altering the actual water/moisture-content via wetting (in water or high humidity environment) or drying, a nice combination of both SME and SCE enables us to tailor the performance of a hydrogel for some special functions, which are not easily achievable based on only the SME or SCE. Similar phenomena have been reported in another hydrogel in [17], which demonstrates the generic nature of this finding.

As shown in Fig. 1(Ia), a hydrogel ball (same as that used in [16], in which the water content in weight fraction in fully wetted gel is more than 15,000%) is able to be easily flattened at above its glass transition temperature (T_g), if it is not very dry [Fig. 1(Ib), two views of a fattened piece from two different angles]. Only upon heating to above its T_g again, the flattened ball is able to almost fully recover its original shape [Fig. 1(Ic)]. On the other hand, if the hydrogel ball is wetted by water inside a straw [Fig. 1(IIa), top], so that its swelling induced expansion is limited in two directions, after it is wetted in room temperature (about 22 °C) water for a week and then removed out of the straw, the ball becomes elliptical shape and only the free expansion axis reaches the same dimension as that of the ball free from any constraint during wetting in water [Fig. 1(IIb)]. The elliptical shaped ball is able to gradually return its original ball shape and size upon drying without leaving any apparent permanent *damage* at all. However, if the straw is with some pre-cuttings, parts of the hydrogel ball may be cut out during swelling [18], since this hydrogel, if wetted in water, becomes brittle and fragile.

Fig. 2(a) compares the sizes of two square shaped hydrogel pieces, one is fully dried and the other is fully wetted. It should be point out that these two pieces have roughly the same size in the dry state. Although this hydrogel, which has been investigated in [17], is different from

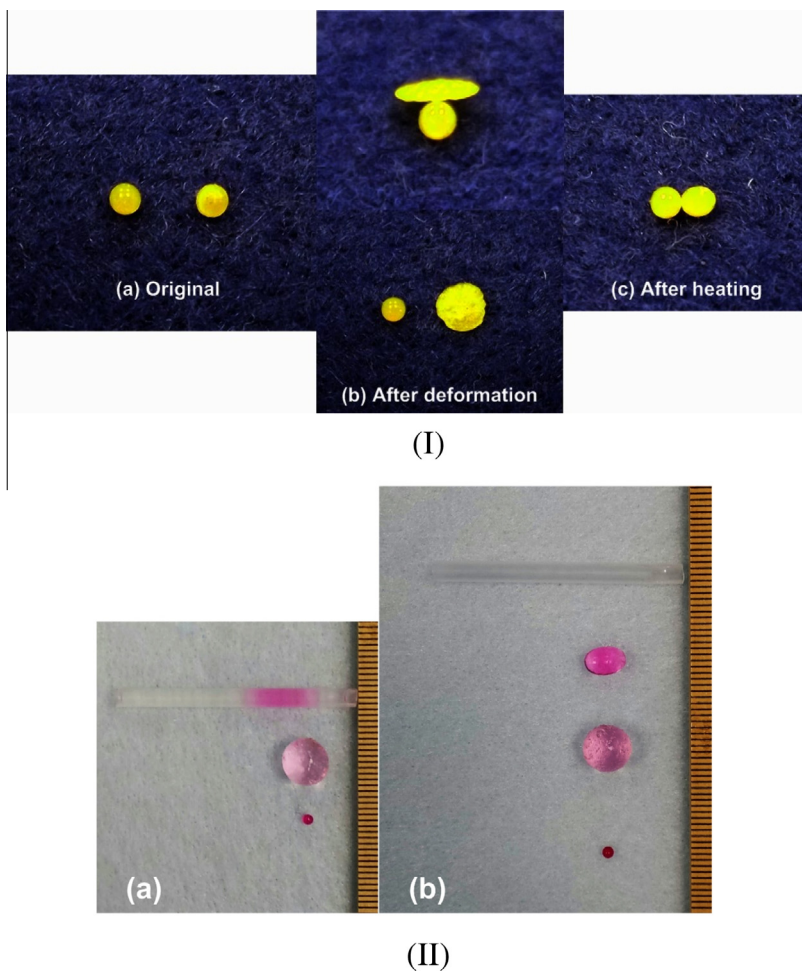
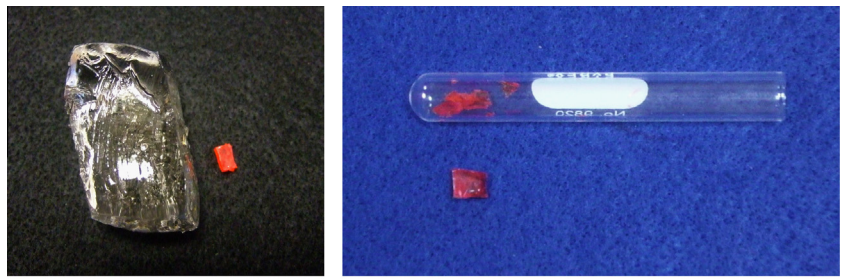


Fig. 1. Heating-responsive SME (I) (another ball without flattening is included for comparison) and swelling with/without constraint (II) in a brittle hydrogel [for comparison, bottom small ball is dry one, and the big ball in the middle is fully wetted in room temperature (about 22 °C) water without any constraint].



(a) (b)

Fig. 2. Comparison of the sizes of a fully wetted and fully dried hydrogels; fractured hydrogel, which has been fully wetted inside a testing tube and then dried (bottom: dry sample outside the tube for comparison) (b). (The hydrogel is the same as that used in [17].)

above mentioned hydrogel ball, both seemingly have about the same swelling ratio. After wetting another piece of square shape hydrogel (approximate same size in the dry state as well) in a testing tube at room temperature for a week and then drying, this piece is fractured into a couple of pieces and becomes unrecognizable (Fig. 2b).

Water/moisture-content dependency of the shape memory/change effect in above two types of hydrogels has been demonstrated in [16,17], but high swelling ratio of both hydrogels upon wetting in water prevents us to observe the water-induced SME. Furthermore, both of them are apparently brittle and fragile after being wetted in water, which limits their applications in some engineering practice.

In this paper, we investigate the shape memory/change effect in a double network nanocomposite hydrogel (DNHG), which is tougher even in its fully wetted state. This double network hydrogel is composed of a rigid and brittle first network interlaced with a loosely crosslinked soft second network, and is usually described as a semi-interpenetrating structure [19]. Such a hydrogel is well known for the high compressive strength, which is water content dependent [20].

The outline of this paper is as following. In Section 2, we introduce the material, sample preparation and main experimental procedures. Section 3 presents experimental results and analysis. Further discussions are carried out in Section 4. Major conclusions of this work are summarized in Section 5.

2. Material, samples preparation and experiments

2.1. Material

The double network nanocomposite hydrogel (PAMPS/PAAm) was synthesized following the procedure reported in [21]. In this hydrogel, silica nanoparticles grafted with vinyl end groups are used as macro-crosslinkers to copolymerize with AMPS, yielding a nanocomposite first network, and subsequent introduction of a secondary PAAm network results in super-tough double-network (DN) composite hydrogels, which do not fracture upon stretching up to 73 MPa and above 98% strain [21].

As fabricated hydrogel was about 6.8 cm thick in the fully wetted state.

2.2. Samples preparation

Different sized samples with different conditions were prepared for a series of experimental investigation. Herein, R_w donates the ratio of the weight of the absorbed water/moisture in a piece of hydrogel to that of the dry state, i.e.,

$$R_w = \frac{W - W_0}{W_0} \tag{1}$$

where W_0 and W are the measured weight of the dry piece and that after wetting in water or within high humidity environment, respectively.

Dry samples were prepared by keeping the hydrogel in an oven at 70 °C for 1 h for *full* water/moisture evaporation. Hence, herein, R_w of the resultant samples is referred as 0; and these samples are named $DNHG_0$. Fully wetted samples were prepared by immersing $DNHG_0$ into room temperature water for 1 day until the water content was stable. R_w of the resultant samples is about 7.5. These samples are named $DNHG_{7.5}$. After exposing $DNHG_{7.5}$ in the open air for 1 day at a relative humidity (RH) of about 50% and room temperature (around 25 °C) for drying, resultant samples were rubber-like and has a R_w of about 0.3. These samples are named $DNHG_{0.3}$. After exposing $DNHG_{7.5}$ in the open air for 3 days at a RH of about 50% and room temperature to dry, R_w of the resultant samples is about 0.05. These samples are named $DNHG_{0.05}$.

Using two pieces of aluminum strips which were prebent into a "S" shape, a piece of "S" shaped hydrogel was cut out of a big piece of fully wetted hydrogel. A piece of "S" shaped $DNHG_{0.05}$ (about 3 mm thick) was obtained after drying in the open air (RH ≈ 50%) at room temperature for 3 days.

2.3. Experiments

An Instron 5569 with a temperature controllable chamber was used for uniaxial compression test. One piece of $DNHG_0$ (≈3 × 3 × 2.4 cm) was compressed at room temperature by 1.2 mm at a strain rate of 4.2%/s to study its mechanical behavior. One piece of $DNHG_{0.3}$ (≈4 × 4 × 3.2 cm), which was in the rubber like state, was compressed at room temperature by 2.5 mm at a strain rate of 3.1%/s, and then unloaded at the same speed. This test was continuously repeated for three times on the

same piece of sample. Another piece of $DNHG_{7.5}$ ($\approx 8 \times 6.3 \times 6.8$ cm) was compressed at room temperature by 4 mm at a strain rate of 1.5%/s, and then unloaded at the same speed. This test was finished after seven continuous cycles on the same sample.

A series of differential scanning calorimeter (DSC) tests were carried out using a DSC-Q200 differential scanning calorimetery at a heating/cooling rate of 10 °C/min for $DNHG_0$, $DNGH_{0.05}$, $DNGH_{0.3}$ and $DNHG_{7.5}$. The purpose of these DSC tests was to investigate the glass transition temperature (T_g) of hydrogel at different wetting conditions. In these tests, the specimens were around 10 mg. Unless otherwise stated, the testing temperature range is normally between about −40 °C and about 100 °C for all samples.

Furthermore, a series of experiments were conducted to investigate the SME in the double network nonocomposite hydrogel.

– **Shape memory effect in $DNHG_0$**

A piece of $DNHG_0$ was placed inside 100 °C silicone oil for 30 s and then deformed using a piece of tweezers. Subsequently, the silicone oil together with the $DNHG_0$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, $DNHG_0$ was put into 100 °C silicone oil again to investigate its heating-responsive behavior.

– **Shape memory effect in $DNHG_{0.05}$**

A piece of $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then bent using a piece of tweezers. Subsequently, the silicone oil together with the $DNHG_{0.05}$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, $DNHG_{0.05}$ was put into 80 °C silicone oil again to check its heating-responsive behavior. A piece of $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then compressed using a one-dollar Singapore coin. Subsequently, the silicone oil together with the $DNHG_{0.05}$ and the coin (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, one water droplet was dropped on the surface. Finally the piece of $DNHG_{0.05}$ was put into 80 °C silicone oil again to study its response. A piece of $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then bent using a piece of tweezers. Subsequently, the silicone oil together with the $DNHG_{0.05}$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, $DNHG_{0.05}$ was put into 80 °C silicone oil again to find its response.

– **Shape memory effect based on swelling**

Another piece of $DNHG_0$ was wetted by a small water droplet on its top surface. The evolution of the surface morphology was observed under a LCD optical microscope (NARSKA,® USA) and recorded in real time. A piece of $DNHG_0$ was bent at high temperatures, and then cooled down with the temporary shape fixed. After that the distorted shape was largely maintained. Then the sample was immersing into room temperature water for full swelling, and then dehydrated in the air. $DNHG_{0.3}$ is highly elastic and one piece of $DNHG_{0.3}$ was bent and held this shape by a clip in the open air for 1 day for dehydration (Fig. 3). After that, the temporary shape was maintained. Another piece of $DNHG_{0.3}$ was dried while being stretched. In the next step, the sample was immersed into room temperature water to check its behavior. The "S" shape $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then straightened using a pair of tweezers. Subsequently, the silicone oil together with the $DNHG_{0.05}$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, half of the $DNHG_{0.05}$ was put into room temperature water to check its response.

– **Heating-responsive SME in $DNHG_{7.5}$ based on melting of water**

A piece of $DNHG_{7.5}$ was pre-bent and then kept in a refrigerator under −20 °C for 1 h. After this, $DNHG_{7.5}$ was taken out and put in the open air at 25 °C to study its response.

3. Results and discussions

3.1. Compression tests

Note that unless otherwise stated, herein, the strain and stress are engineering strain and engineering stress.

As shown in Fig. 4(a), during compression $DNHG_0$ cracked continuously, evidenced by multiple drops in the stress vs. strain curve during compression. Eventually as shown in Fig. 4(b), $DNHG_0$ was split into small pieces.

Fig. 5(a) shows the result of $DNHG_{0.3}$ in three loading–unloading cycles (uniaxial compression) at room temperature. Virtually we cannot see any difference in the resulted curves in these three cycles. Fig. 5(b) shows the result of $DNHG_{7.5}$ in seven loading–unloading (uniaxial compression) cycles as room temperature. It is easy to see the difference after one cycle. In the subsequent six cycles, the curves become nonlinearly elastic and without any hysteresis (Fig. 5b). It was noticed that probably some water was pressed out of the hydrogel during the first compression cycle, which might be the causes of the

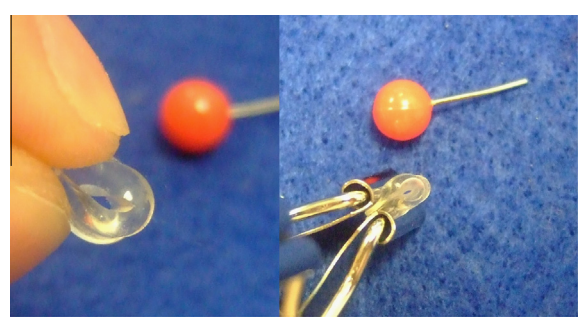


Fig. 3. Bending rubber-like $DNHG_{0.3}$.

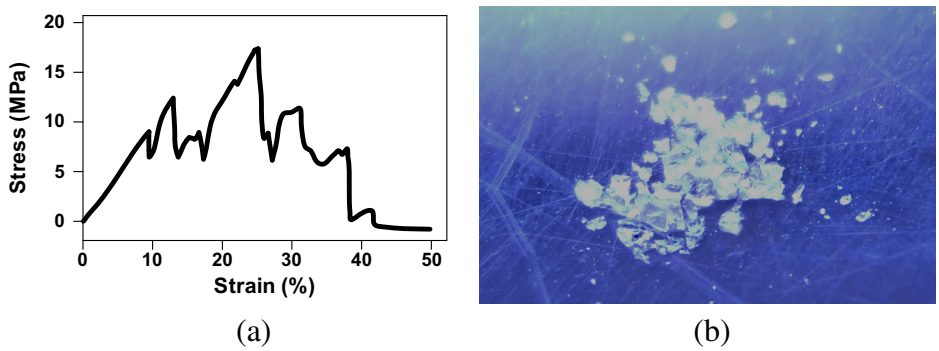


Fig. 4. Compression stress vs. compression strain relationship of $DNHG_0$ (a); morphology after 50% compression (b).

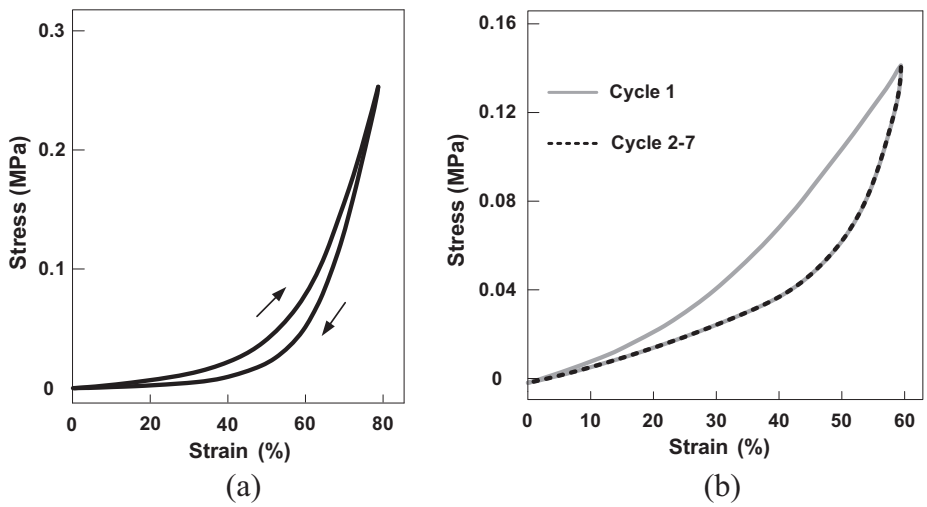


Fig. 5. (a) Compression stress vs. compression strain relationship of $DNHG_{0.3}$ in three loading–unloading cycles; (b) compression stress vs. compression strain relationship of $DNHG_{7.5}$ in seven loading–unloading cycles.

difference between the curve in the first cycle and those in the following six cycles. As compared with the compression stress in Fig. 4, in Fig. 5(a and b), for about the same compression strain, the compression stresses of $DNHG_{0.3}$ and $DNHG_{7.5}$ are about the same level, but much lower than that of $DNHG_0$.

3.2. Thermal analysis

Fig. 6 plots the DSC results of hydrogels with different R_ws. Note that due to the possible non-uniformity nature of water/moisture distribution within this double network nanocomposite hydrogel, R_ws determined here are essentially nominal.

For $DNHG_0$, the glass transition is at around 80 °C. With the increase of water content, the glass transition shifts to a lower temperature range. It appears that for $DNHG_{7.5}$, the glass transition is hardly observable. A *melting* transition is spotted at around 5 °C upon heating and the corresponding *freezing* transition is at about −18 °C upon cooling. It is noticed that during freezing the sample releases heat at a

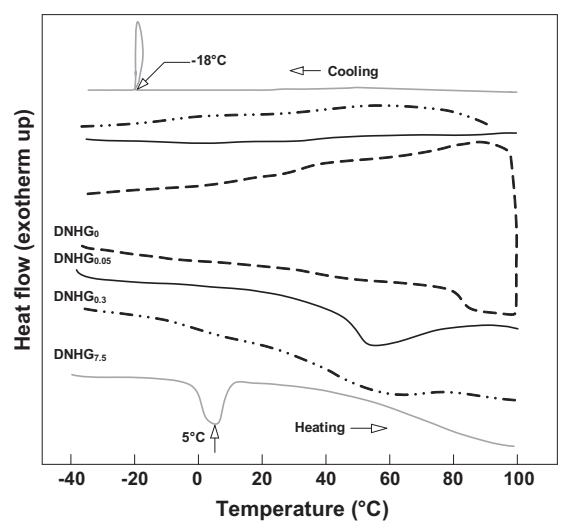


Fig. 6. DSC results of hydrogels with different R_ws.

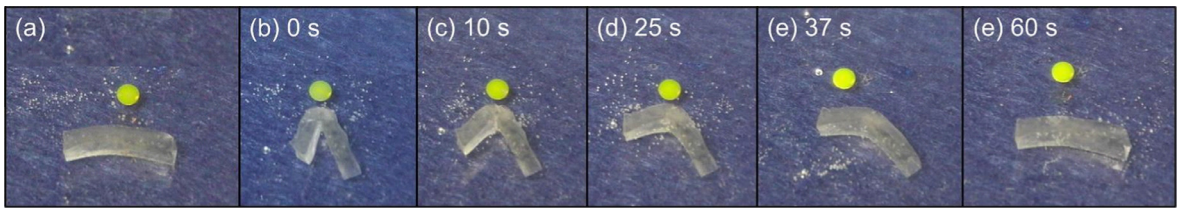


Fig. 7. Heating-responsive SME in $DNHG_0$. (a) Original shape; (b) after bending at 100 °C; (c–e) recovery sequence in 100 °C silicone oil.

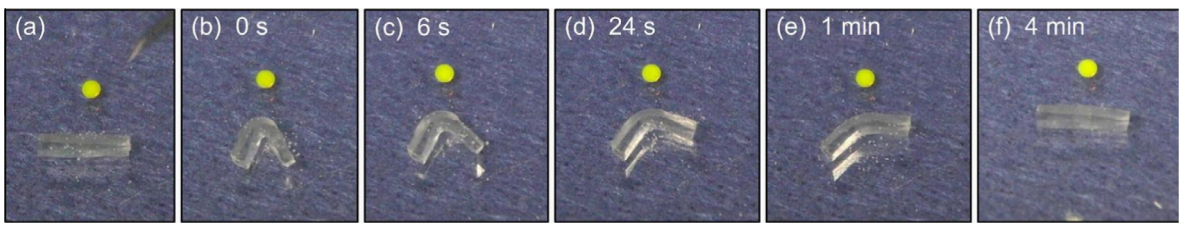


Fig. 8. Heating-responsive SME in $DNHG_{0.05}$. (a) Original shape; (b) after bending at 80 °C; (c–f) subsequent of recovery upon immersing into 80 °C silicone oil.

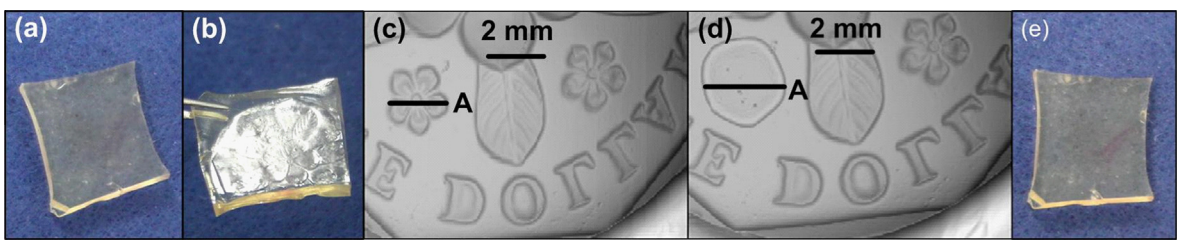


Fig. 9. Heating-responsive SME in $DNHG_{0.05}$. (a) Original shape; (b) after impression; (c) 3-D scanned morphology; (d) 3-D scanned image 3 h after a droplet was applied on the right flower; (c) after immersing into 80 °C silicone oil.

very high fast, so that a closed-loop feature appears in the curve at around 18 °C.

3.3. Shape memory effect

– **Heating-responsive shape memory effect in $DNHG_0$**

As shown in Fig. 7, $DNHG_0$ (≈3 × 3 × 9 mm) was immersed into 100 °C silicone oil for 30 s and then bent using a piece of tweezers. After the sample together with the silicone oil was cooled down to room temperature (with the temporary shape being fixed), a temporary shape was resulted. Upon immersing into 100 °C silicone oil again, $DNHG_0$ recovers its original shape within 60 s.

– **Heating-responsive shape memory effect in $DNHG_{0.05}$**

In Fig. 8, $DNHG_{0.05}$ (≈3 × 3 × 8 mm) was immersed into 80 °C silicone oil for 30 s and then bent using a piece of tweezers. The temporary shape was resulted after the sample together with the silicone oil was cooled down to room temperature (with the temporary shape being fixed). $DNHG_{0.05}$ recovers its original shape within 4 min upon immersing into 80 °C silicone oil again.

Another piece of $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then compressed using a one dollar

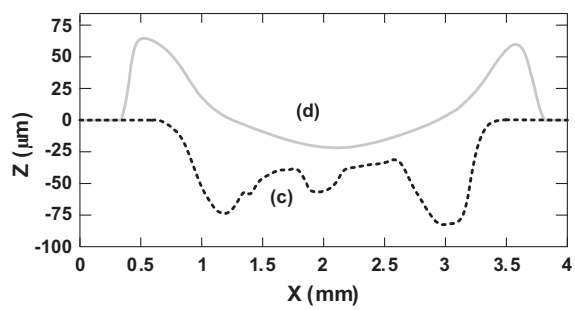


Fig. 10. Comparison of surface profile along the lines marked in Fig. 9(c and d).

Singapore coin. After the sample and coin together with the silicone oil were cooled down to room temperature (with the temporary shape being held), the impression of the coin was left on the hydrogel (Fig. 9b and c). A small water droplet was dropped on the right flower marked as A in Fig. 9(c). Three hours later the flower shape disappeared (Fig. 9d). The surface profiles along the marked lines in Fig. 9(c) and (d) are compared in Fig. 10. It appears that the features inside of the flower are largely removed,

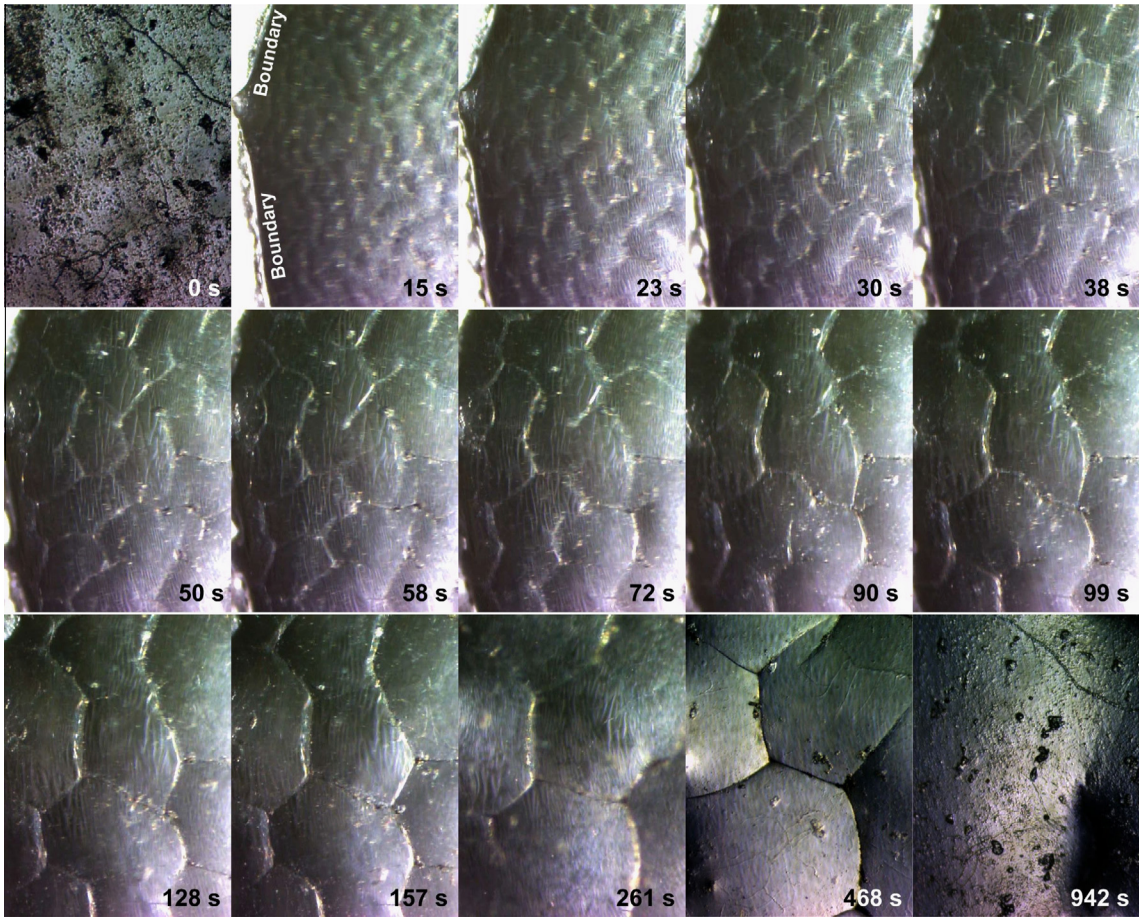


Fig. 11. Wetting by one small water droplet (vertical size of each image is about 1 mm).

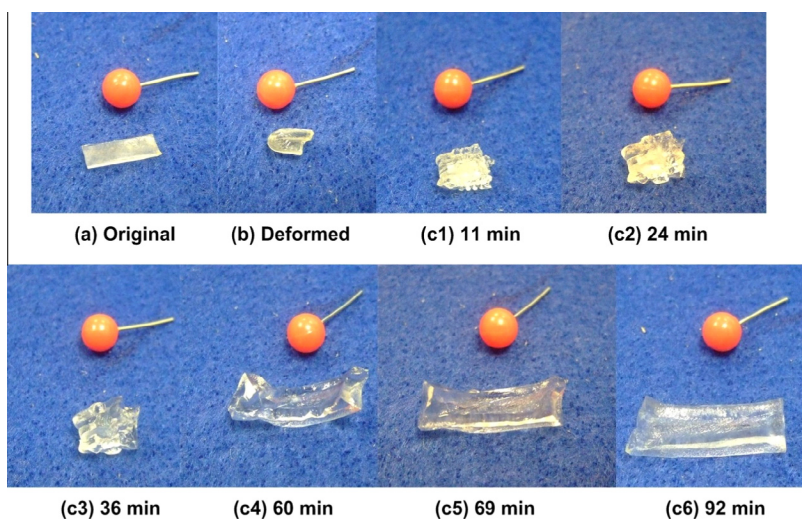


Fig. 12. Low swelling ratio tough hydrogel ($DNHG_0$) upon wetting in water. (a) Original shape; (b) after being deformed at high temperatures; (c1–c6) upon wetting in room temperature water.

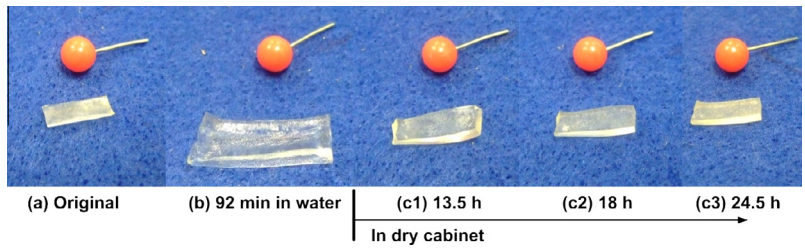


Fig. 13. Dehydration of the swelled hydrogel in Fig. 12(c6).

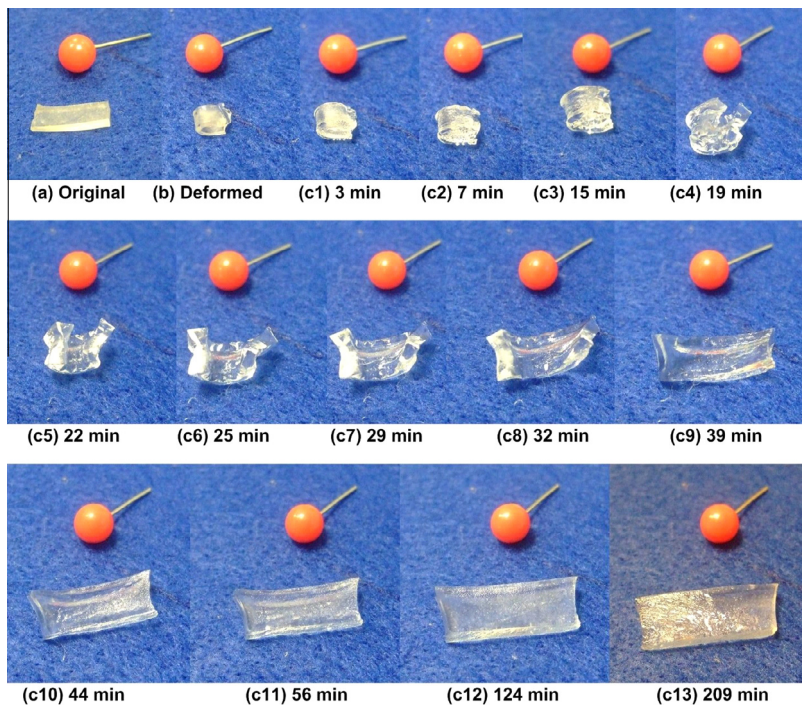


Fig. 14. SME based on swelling. (a) Original shape; (b) after being bent and dehydrated; (c1–c13) shape recovery upon swelling.

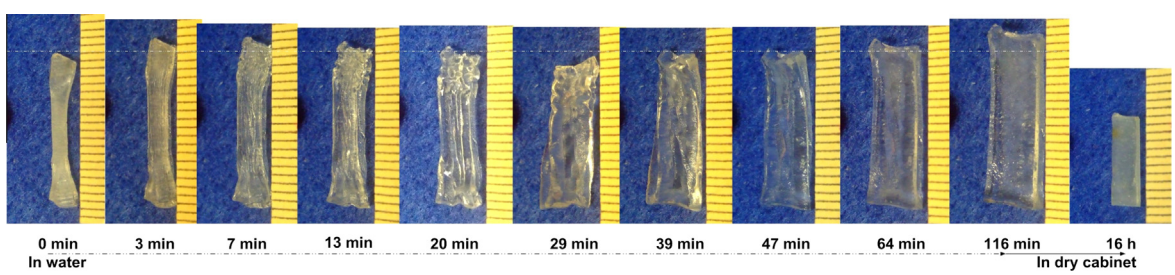


Fig. 15. The SME during swelling in water in a pre-stretched sample.

while the boundary of the water droplet forms a protrusive circle, about 70 μm above the base surface. Note that 3D surface scanning was conducted using a Talyscan Universal. The surface of the hydrogel became flat again within a few seconds upon immersing into silicone oil for one more time (Fig. 9e).

– **Shape memory effect based on swelling**

A piece of $DNHG_0$ was wetted by a small water droplet on its top surface. The evolution of the surface morphology was observed and recorded in real time. Snapshot is presented in Fig. 11. As we can see, after wetting by water

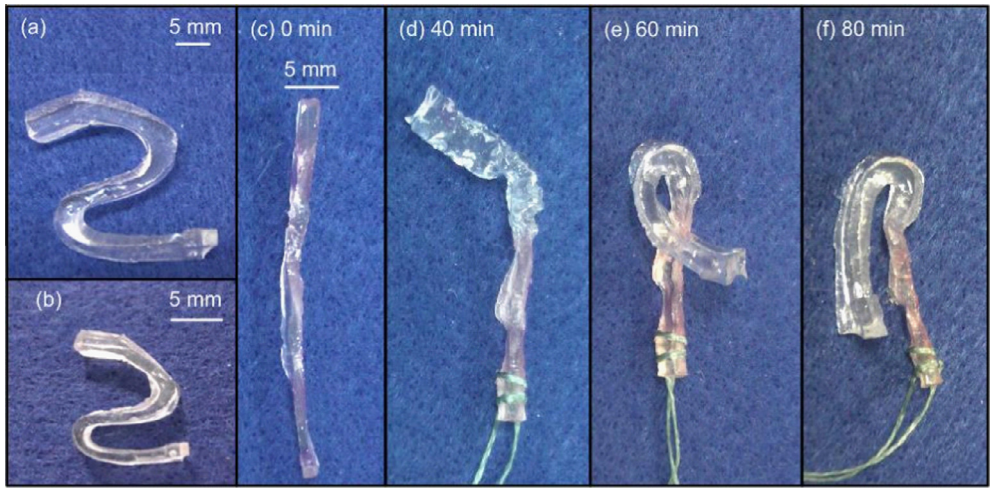


Fig. 16. The SME based on wetting in water. (a) Original shape; (b) after being dried in the open air at room temperature; (c) after being straightened in silicone oil at 80 °C and cooled; (c–f) shape recovery of the top half upon immersing it into room temperature water.

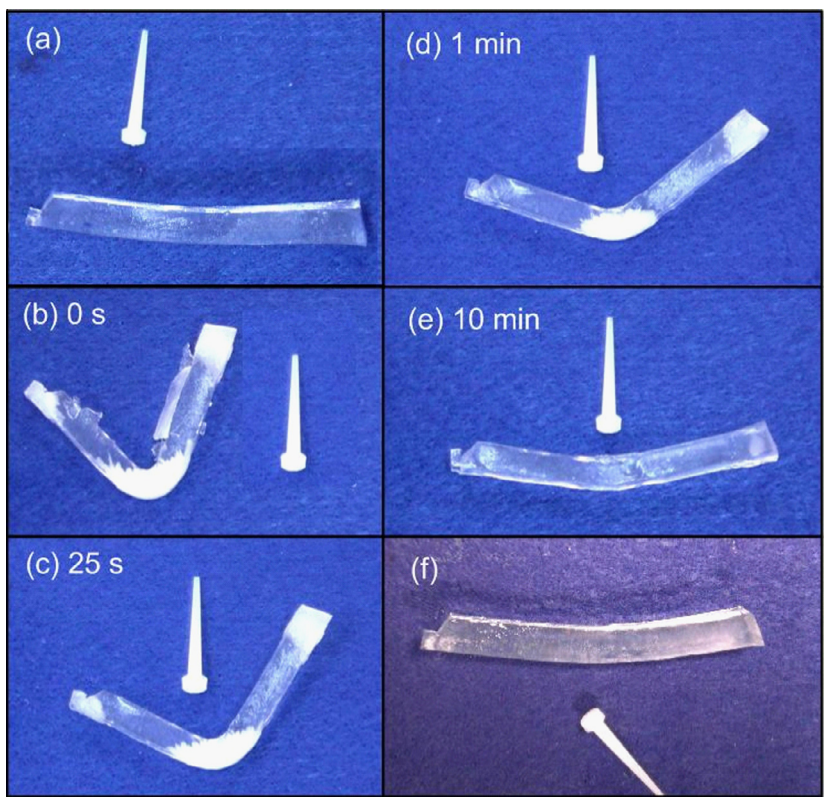


Fig. 17. Heating-responsive SME based on melting of water in $DNHG_{7.5}$. (a) Original shape; (b) after being bent and kept at −20 °C for 1 h; (c–e) shape recovery sequence at around 25 °C; (f) after being immersed in room temperature water for 30 min.

droplet, small *protrusions* emerge at about 15 s and then grow. Subsequently, small *protrusions merge* together to form bigger ones. After a while, *protrusions* start to disappear. At 942 s, the surface morphology virtually returns back to the original one. The features, which merged and then disappeared, are due to swelling induced buckling phenomenon as well explained in [17].

In this type of hydrogel, which is tough and has limited swelling ratio, water/moisture-induced shape recovery can be observed upon wetting in water only. Limited swelling

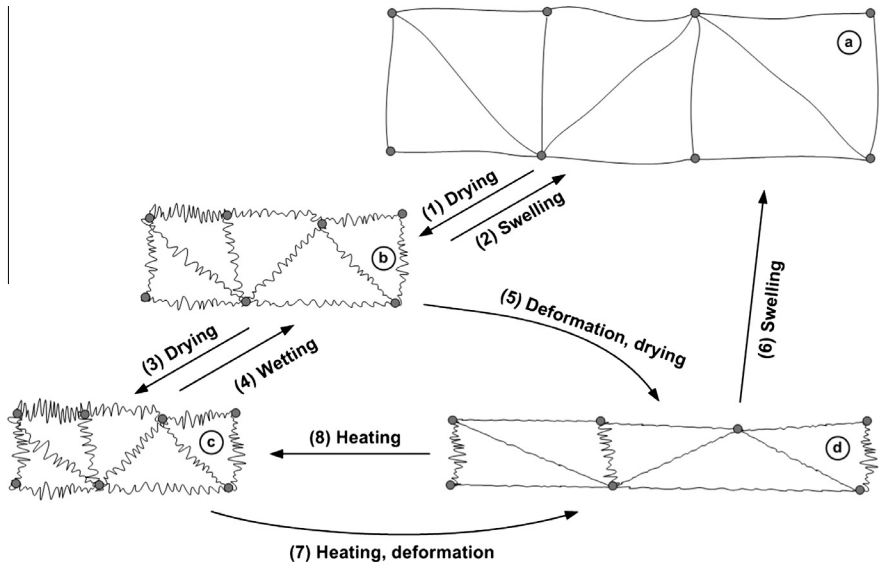


Fig. 18. Moisture/water content dependent response of hydrogel. (a) Fully swelled; (b) wet shape without apparent swelling; (c) dry shape; (d) deformed temporary shape.

ratio provides us a chance to observe the water-responsive SME.

As shown in Fig. 12, after being immersed into room temperature water, the pre-bent $DNHG_0$ ($\approx 1 \times 4 \times 10$ mm) swells and in the mean time returns its original shape (Fig. 12c). After dehydration in a dry cabinet (35% RH, 25 °C), the piece of hydrogel recovers its original shape and size (Fig. 13).

As compared with the hydrogels investigated in, for instance [16], now we may conclude that depending on the actual swelling ratio and swelling speed in a particular hydrogel, wetting by moisture (without significant swelling) or water (remarkable swelling) may result in remarkably different response.

Based on the high elasticity of $DNHG_{0.3}$, another experiment was carried out to confirm its water-responsive SME (Fig. 14). After being distorted and dehydrated, the temporary shape of $DNHG_{0.3}$ ($\approx 1 \times 4 \times 10$ mm) was maintained (Fig. 14b). 209 min after being immersed into room temperature water for wetting, the distorted shape of this piece of hydrogel disappears (Fig. 14-c13).

Another piece of $DNHG_{0.3}$ ($\approx 1 \times 3 \times 11$ mm) was stretched and then dehydrated to fix the temporary shape. After being immersed into room temperature water, we can see the sample starts to absorb water and swell (from 3 min to 7 min in Fig. 15). Then it starts to contract upon further wetting (from 13 min to 29 min in Fig. 15). From 29 min to 116 min in Fig. 15, the sample restarts to expand continuously until being fully wetted. After subsequent dehydration in the air for 16 h, the sample recovers its original shape again. The observed contraction phenomenon upon wetting in water is obviously due to the water-induced SME, which is hard to be observed in hydrogels with a very high swelling ratio.

The "S" shaped $DNHG_{0.05}$ was placed inside 80 °C silicone oil for 30 s and then straightened using a pair of tweezers. The temporary shape was fixed after the silicone oil together with the $DNHG_{0.05}$ was gradually cooled down to room temperature in the air (Fig. 16c). After this, half of the "S" shaped $DNHG_{0.05}$ was put into room temperature water, so that this part gradually recovered its original shape upon wetting (Fig. 16d–f), while the other half maintained its temporary shape. Unlike that of wetting poly (methyl methacrylate) (PMMA) in ethanol [22], which has a clear *dry/wet* boundary and follows the case II theory of diffusion, here the transient wet/dry boundary even after 80 min of wetting in water is still gradual.

– **Heating-responsive SME in $DNHG_{7.5}$ based on melting of water**

As shown in Fig. 17, a piece of $DNHG_{7.5}$ ($\approx 6 \times 6 \times 50$ mm) was bent and kept at −20 °C for 1 h. Subsequently, the temporary shape was fixed (Fig. 17b). After exposing in air (around 25 °C) for 10 min, the water in the hydrogel gradually melts (refer to Fig. 6), and shape recovery was largely achieved as revealed in Fig. 17(e). However, in comparison with the original shape, there is still some difference, which should be mainly because of water lost in compression upon bending (refer to the discussion in Section 3.1). Only after being immersed into room temperature water for 30 min, the hydrogel almost fully recovered its original shape (Fig. 17f).

4. Further discussions

Above experiments confirm the influence of water content on the shape memory/change effect in hydrogels. However, unlike the hydrogels studied in [16,17], which have a high swelling ratio but brittle after being wetted in water, this hydrogel is tough (even in the full swelling

state) and has a much lower swelling ratio. Hence, this tough gel has some unique features, which are normally unachievable in ordinary non-tough hydrogels. These features include,

- Since the glass transition is still applicable, the dry hydrogel has the heating-responsive SME.
- Since this tough hydrogel is tough even in its full wet state, we are able to not only deform fully wetted hydrogel for the mechano-responsive SCE (rubber-like) or for subsequent drying to fix the temporary shape, but also utilize the absorbed water as the transition component for the heating-responsive SME.
- High humidity is not enough either to induce moisture-induced shape recovery and nor to cause remarkable swelling.
- Lower swelling ratio of this tough hydrogel enables us to clearly reveal the water-induced shape recovery, which is normally hard to see in hydrogels with a higher swelling ratio.

Except the heating-responsive SME based on the absorbed water as the transition component, all other SME/SCE features of this hydrogel may be schematically summarized as shown in Fig. 18. Let us start from (a), which is fully swelled gel. Upon drying (1), it shrinks to (b). Upon further drying (3) to (c), the volume change is relatively ignorable. Upon partial wetting in water (4), i.e., (c) to (b), there is no significant volume change, but the gel changes from hard to viscous elastic or rubber-like (depending on the actual amount of water content), i.e., the mechano-responsive SCE. Further wetting in water (2), the gel swells remarkably. A combination of steps (1) and (2) is the water-responsive SCE. (d) Maybe reaches from (a), (b) or (c). But the latter two are practically more accessible. We may either stretch (b) and then dry it (5), or heat (a) and then stretch it to produce (d) (7). Heating (d) results in (c) ((8), heating-responsive SME). Wetting (d) in water produces (a).

5. Conclusions

A systematic investigation is carried out to study the shape memory/change effect in a tough hydrogel. Water-content dependency of the response of this hydrogel to heating and wetting is confirmed. Since this hydrogel is tough (even after being fully wetted in water) and has a relative lower swelling ratio, additional novel features, such as heating induced SME using absorbed water as the transition component, mechano-responsive shape change effect (SCE) and water-induced SME, which are not possible for many brittle hydrogels with a higher swelling ratio, have been achieved.

The influence of water/moisture content on the T_g, which is the underlying mechanism for the water-induced SME in hydrogels with a relative lower water-content and rubber-like mechano-responsive SCE in hydrogels with a relative higher water-content, is confirmed. Since the glass transition exists in the dry state, this hydrogel still has the heating-responsive SME even it is fully dried.

Based on this study, the change in microstructure during deformation, wetting in water/drying and heating etc. is schematically illustrated as a clear road map for a better understanding of various phenomena and their corresponding mechanisms in this tough hydrogel.

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